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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the nonaqueous electrolyte secondary battery provided with the anode containing a lithium content multiple oxide, the negative electrode which includes a dope and the carbon material which can be dedoped for a lithium ion, and the nonaqueous electrolyte which dissolves a lithium salt electrolyte in a nonaqueous solvent. It is related with the nonaqueous electrolyte secondary battery where especially improvement of electrolyte composition was made and which was excellent in the low-temperature characteristic and a cycle characteristic.

[0002]

[Description of the Prior Art]In recent years, the miniaturization of a portable device follows on progressing and the demand of the miniaturization and the weight saving is increasing to the cell used as the power supply. Advanced features of apparatus follow on progressing, power consumption increases, and the demand to that charge is completed to a cell for a short time and discharge of a heavy load being possible is increasing. The nonaqueous electrolyte secondary battery which considers a lithium ion as a dope and uses as a negative electrode the carbon material which can be dedoped as what meets the demand of a small weight saving attracts attention, and it inquires briskly. Especially the nonaqueous electrolyte secondary battery that used the polymer gel electrolyte for the electrolyte to the demand of slimming down is dramatically suitable. In service temperature environment, it is high ion conductivity until now as an electrolyte, and since the solvent boiling point is high and the vapor rate is slow, carbonic ester is used as a main solvent. However, when it is used with the electrolysis solution solvent independent, since viscosity is high and the ionic conductivity in low temperature falls, the fall of a battery characteristic may arise. In order to solve such a problem, low viscosity solvents, such as dimethyl carbonate and diethyl carbonate, are used.

[0003]However, low viscosity solvents, such as chain carbonic ester, are low-boiling point solvents in many cases, a low-boiling point solvent may volatilize at the time of cell production, and battery capacity may fall by expansion of a cell, modification of the cell shape by the rise of inter cell pressure, or reduction of the amount of solvents. However, it is dramatically difficult to raise the low-temperature characteristic, without using a low viscosity solvent.

[0004]

[Problem(s) to be Solved by the Invention]The anode which this invention tends to solve the above-mentioned problem and contains a lithium content multiple oxide, Let it be a key objective to raise the low-temperature

characteristic and a cycle characteristic in the nonaqueous electrolyte battery provided with the negative electrode which includes a dope and the carbon material which can be dedoped for a lithium ion, and the nonaqueous electrolyte which dissolves a lithium salt electrolyte in a nonaqueous solvent.

[0005]

[Means for Solving the Problem] This invention a dope, an anode which can be dedoped, a metal lithium negative electrode, or a lithium ion for a lithium ion A dope and a negative electrode which can be dedoped, It is the cell provided with nonaqueous electrolyte which dissolves a lithium salt electrolyte in a nonaqueous solvent, By considering it as a nonaqueous electrolyte battery, wherein this nonaqueous solvent contains a cyanoethoxy compound expressed with general formula $R-(OC_2H_4CN)_n$, a charging and discharging characteristic and a cycle characteristic in low temperature can be raised.

[0006] Here, $n = 1-4$ and R are any one of the following structures among the above-mentioned formula.

[0007] R: $H_{2m \text{ of } C_m + 2-n}$ and $H_{2m \text{ of } C_m + 2-n}(OC_2H_4)_p$, $H_{2m \text{ of } C_m + 2-n}CO$, and $H_{2m \text{ of } C_m + 2-n}OCO$ ($m = 1-3$, $p = 1-4$)

[0008]

[Embodiment of the Invention] Hereafter, this invention is explained concretely. According to this invention, the thing of the multiple oxide of lithium, the multiple oxide of cobalt and lithium, the multiple oxide of nickel and lithium, and manganese or the above-mentioned multiple oxide which replaced cobalt, nickel, and manganese in part with other transition metals, respectively can be used as an anode, for example. As a chargeable and dischargeable negative pole material, a carbon material can be used for a lithium ion. As a supporting electrolyte of an electrolysis solution. ** $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiSO_3CF_3$, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiN(SO_2CF_3)_3$ lithium salt, such as $Li(SO_2CF_3)_3$, -- independence -- or two or more sorts can be mixed and it can use $(SO_2C_4F_9)$. As a nonaqueous electrolyte solvent, for example Methylcyanoethyl ether,

ethylcyanoethyl ether, Dicyanoethyl ether, ethylene glycol cyanoethyl ether, Cyanoethoxy compounds, such as methylcyano ethyl ester, ethylcyano ethyl ester, and methylcyanoethyl carbonate, independence, Or if two or more sorts of solvents (for example, ethylene carbonate, propylene carbonate, a gamma butyrolactone, etc.) including solvents other than the above are mixed and used, it can **. Thereby, the low-temperature characteristic and the cycle characteristic of a nonaqueous electrolyte secondary battery can be raised.

[0009] As a reason such an effect is acquired, it thinks as follows. That is, the fall of the mobility of the lithium ion at the time of the low temperature by the rate of high viscosity of nonaqueous electrolyte can be considered as one of the causes of the low-temperature characteristics degradation of a nonaqueous electrolyte secondary battery. A coagulating point and a coefficient of viscosity are low, and a cyanoethyl ether compound does not bar movement of a lithium ion under low temperature. Since the dielectric constant is high, the degree of disassociation of a lithium salt electrolyte is large, and contributes to improvement in ionic conductivity. In addition, it is suitable, when it is hard to volatilize in a production process, it is made a sheet shaped like especially a gel electrolyte and it assembles, since the boiling point is very as high as not less than 150 ** as compared with other low viscosity solvents, such as chain carbonic ester. Although these cyanoethoxy compounds are concretely shown in Table 1, this invention is not limited to this.

[0010]

[Table 1]

化合物	名 称	構 造 式
1	メチル2-シアノエチルエーテル	$\text{CH}_3 \text{ OC}_2 \text{ H}_4 \text{ CN}$
2	エチル2-シアノエチルエーテル	$\text{C}_2 \text{ H}_5 \text{ OC}_2 \text{ H}_4 \text{ CN}$
3	エチレングリコールエチルシアノエーテル	$\text{C}_2 \text{ H}_5 \text{ OC}_2 \text{ H}_4 \text{ OC}_2 \text{ H}_4 \text{ CN}$
4	ビス-2-シアノエチルエーテル	$\text{NCC}_2 \text{ H}_4 \text{ OC}_2 \text{ H}_4 \text{ CN}$
5	ビス-2-シアノエトキシエチレングリコール	$\text{NCC}_2 \text{ H}_4 \text{ OC}_2 \text{ H}_4 \text{ OC}_2 \text{ H}_4 \text{ CN}$
6	メチル2-シアノエチルエステル	$\text{CH}_3 \text{ COOC}_2 \text{ H}_4 \text{ CN}$
7	エチル2-シアノエチルエステル	$\text{C}_2 \text{ H}_5 \text{ COOC}_2 \text{ H}_4 \text{ CN}$
8	メチル2-シアノエチルカーボネート	$\text{CH}_3 \text{ OCOOC}_2 \text{ H}_4 \text{ CN}$
9	ビス2-シアノエチルカーボネート	$\text{NCC}_2 \text{ H}_4 \text{ OCOC}_2 \text{ H}_4 \text{ CN}$

[0011]

[Example] Hereafter, although an example explains the details of this invention, this invention is not limited to this.

[0012] The sheet-shaped cell of this invention was produced according to the following procedure.

[0013] (Production of an anode) Carbon 10 weight section was mixed as LiCoO_2 87 weight section and a conducting material as positive active material, polyvinylidene fluoride 3 weight section was mixed as a binder, positive electrode mixture was adjusted, N-methyl-2-pyrrolidone was made to distribute this, and the positive electrode mixture slurry was adjusted. Next, after applying this slurry to one side of the aluminium foil of the 20-micrometer thickness which is a positive pole collector uniformly, the sheet shaped positive electrode was obtained by drying and performing compression molding with a roll press machine.

[0014] (Production of a negative electrode) Polyvinylidene fluoride 6 weight section which are 94 weight sections and a binder about a carbon material was mixed as negative electrode active material, it was considered as negative electrode mixture, N-methyl-2-pyrrolidone was distributed, and the negative electrode mixture slurry was adjusted. Next, after applying this slurry to one side of copper foil of the 20-micrometer thickness which is a negative pole collector uniformly, the sheet-shaped negative electrode was obtained by drying and performing compression molding with a roll press machine.

[0015](Production of a nonaqueous electrolyte secondary battery) LiBF_4 was dissolved in the mixed solvent of 1 sort of cyanoethoxy compound 60 capacity % and ethylene carbonate 40 capacity % which were chosen from the compounds 1-9 shown in Table 1 so that it might become 1 mol/l as a supporting electrolyte, and nine kinds of electrolysis solutions were prepared for it.

[0016]In each above-mentioned electrolysis solution, polyethylene oxide 3 organic-functions acrylic ester was mixed so that a weight ratio with this electrolysis solution might be set to 1:4. The gel electrolyte was formed by impregnating a 30-micrometer-thick polypropylene nonwoven with this mixed liquor individually, and irradiating with an electron beam. After pasting together above-mentioned anode / gel electrolyte / negative electrode, from the anode and the negative electrode, the lead was drawn and it obturated using the aluminum lamination. The thin nonaqueous electrolyte secondary battery of this inventions 1-9 as this shows to drawing 1 was produced.

[0017]It is in drawing 1 and, as for a separator and 4, a positive pole collector and 2 are [a negative pole collector and 6] aluminum laminations a negative electrode and 5 an anode and 3 1.

[0018](Comparative example) The nonaqueous liquid rechargeable battery of the comparative example was produced on the same conditions except having changed into the gamma butyrolactone the cyanoethoxy compound in the electrolysis solution used for an above-mentioned gel electrolyte.

[0019]The temperature-characteristics examination of the cell of this invention and the cell of a comparative example was done, and the rate of service capacity over theoretical capacity was shown in Table 2.

[0020]

[Table 2]

	2 0 ℃放電容量	- 1 0 ℃放電容量
本發明 1	9 9 . 3 %	8 5 . 0 %
本發明 2	9 8 . 5 %	8 4 . 6 %
本發明 3	9 7 . 0 %	8 3 . 5 %
本發明 4	9 7 . 4 %	8 3 . 9 %
本發明 5	9 6 . 5 %	7 9 . 4 %
本發明 6	9 8 . 8 %	8 4 . 8 %
本發明 7	9 7 . 6 %	8 4 . 1 %
本發明 8	9 6 . 7 %	8 0 . 0 %
本發明 9	9 5 . 8 %	7 9 . 2 %
比較例	9 5 . 4 %	7 7 . 0 %

[0021]The result of Table 2 shows that the low-temperature charge-and-discharge performance at -10 ** has been improved as compared with the cell of a comparative example by which the nonaqueous electrolyte secondary battery of this invention using a cyanoethoxy compound used only conventional cyclic carbonate as a nonaqueous solvent.

[0022]Next, at the temperature of 20 **, the cycle test which charges and discharges on condition of the final voltage 2.70V by 15 mA of discharge current continuously on the conditions of charging time 3 hours according to the charge voltages 4.10V and 37.5 mA of charging current was done using the cell of this invention 1, and the cell of a comparative example. The result is shown in drawing 2.

[0023]As for it, a passage clear from drawing 2 turns out that the cell of this invention 1 is excellent in a cycle characteristic compared with the cell of a comparative example.

[0024]

[Effect of the Invention]In the nonaqueous electrolyte secondary battery provided with the anode which contains a lithium content multiple oxide according to this invention, the negative electrode which includes a dope and the carbon material which can be dedoped for a lithium ion, and the nonaqueous electrolyte which dissolves a lithium salt electrolyte in a nonaqueous solvent, Being able to improve the low-temperature characteristic and a cycle characteristic, the industrial value is size.

[Translation done.]